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OF THE

NATIONAL SPELEOLOGICAL SOCIETY

VOLUME 30 NUMBER 1

Contents

CAVE DEVELOPMENT VIA SULFURIC ACID

RECENT VERTEBRATES FROM ONTARIO, CANADA

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JANUARY 1968

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Cave Development Via the Sulfuric Acid Reaction

By David F. Morehouse

ABSTRACT

Data from chemical analyses conducted on the waters of Level Crevice Cave, Dubuque, Iowa, support the hypothesis that the major solution reaction occurring in and around the cave, and therefore, locally in the Galena dolomite, involves sulfuric acid, not carbonic acid. This knowledge is extremely valuable to the speleologist involved in the determination of cave origin and development, and concomitantly with the explanation of both the normal and the anomalous features of the cave(s) in question.

INTRODUCTION

Until recently, the majority of the work accomplished in speleogenesis has consisted of qualitative observation of cave phenomena. During recent years, however, a growing number of speleologists, c.f. Davies (1951), Holland (1964) and others, have concluded that these qualitative observations, while quite important, are necessarily limited in their resolving power, and that the time has come to test our previous ideas and to extend our ability to develop new ones, on the basis of detailed quantitative observation. It is on this basis that this research was conceived and conducted.

Beginning January 1, 1964, the Iowa Grotto undertook a detailed reconnaissance and survey of the numerous caves located within, and in close proximity to, the City of Dubuque, Dubuque County, Iowa. As a part of this survey, the author conducted chemical analyses on the waters of Level Crevice Cave to determine the character of the major solution and deposition reactions, in the firm belief that analysis of the data gained would be indispensable to any consideration of the speleogenesis of Level Crevice Cave in particular, and of the Dubuque area caves developed in the Galena Formation in general.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the entire membership of the Iowa Grotto, a chapter of the National Speleological Society, without whose assistance in the field this research would have been impractical. Particularly, thanks go to Richard K. Lewis and James A. Dockal, who have accompanied me on nearly all sample collecting trips, and to Albert A. Jagnow, who so often made the sacrifice of remaining "uptop" so that those of us who went underground could return to the surface safely.

In addition, special thanks go to Dr. Donald McDonald of the University of Iowa, for many helpful suggestions, bacterial identifications, and the use of his laboratory facilities.

PREVIOUS WORK

The Dubuque caves are located in the Tri-State mining district, and were mined in a series of intensive "booms" from 1788 until about 1914 for their lead and zinc sulfide ores. As a result of this mining, the great majority of the caves were opened to the surface for the first time, either through adits, or more usually through vertical shafts.

Many of the location data on these mined caves were compiled by the United States

Geological Survey during an extensive study of the Dubuque area from 1951 to 1957, principally by Whitlow and Brown (1963). In addition to location data, general information on the mines was gathered, and most importantly, the geology and mineralogy of the area were delineated on an up-to-date basis.

Pertinent speleological research on the Dubuque cave area includes that of J Harlen Bretz (1938) and Alan D. Howard (1960). In addition, the author presented a paper on the solubility of the dolomite bedrock in water at the 1965 National Speleological Society Convention (Morehouse, 1965).

Level Crevice Cave

The site of the solution chemistry survey, Level Crevice Cave, is beneath sections 21, 22, and 23 of the U.S.G.S. Dubuque North Quadrangle. The cave is developed in Galena dolomite, of Middle Ordovician age, on three vertically separated and parallel levels, for a distance of 1½ miles along the controlling joint, which trends N. 89° E., making the cave passages nearly perpendicular to the Mississippi River, two miles east of the cave.

The cave was mined for lead sulfide ore (galena) from about 1840 to about 1880. From 1880 to 1907 the city used the cave as a catchment area and storage reservoir for its water supply, installing a dam at the bottom of Rose Shaft in Level C. This dam is shown, along with other pertinent information, on the cave map (figure 1), which represents the passage from the Eastern Entrance to the Dirt Slope, including approximately one-half of the total length of the cave, and encompassing the area within which water samples were taken. Entry to the cave is gained either by the Eastern Entrance, or by Rose or Whipsey shafts.

Important minerals found in the cave are calcite, pyrite, marcasite, galena, and limonite. The bedrock is dolomite.

Speleogenic Features

The cave exhibits pronounced joint control, as may be seen on the cave map. The cave passages also appear to have been controlled by development at favorable stratigraphic levels, as noted by Howard (1960), due to:

1) Differential fracturing and brecciation of the bed rock, and
2) Variable solubility of the bedrock due to differences in porosity and chemical composition.

All passages where the wall rock is unaltered by mining exhibit a large number of uncommonly fresh and clear phreatic features, including interconnected levels, passages closely following the stratigraphy and structure, rock bridges, crude boxwork, chimneys, ceiling pockets, spongework, solution pitting, and a network pattern in the side passage complexes.

The vadose features of the cave include streams due to dams, one in the first right-hand side passage in Level A west of Whipsey Shaft, and the other east of the valve in the Level C dam. These streams are obviously secondary, due to their human origin.

In Level B, which has been drained and partially explored by the Iowa Grotto since work began in the cave in 1964, small ceiling channels and roof pendants are found, which apparently formed during this secondary invasion. All dripstone and flowstone speleothems are confined to Level A, with the exception of those in Level C east of the dam.

The other interesting speleogenic feature of the cave, as will be seen later, cannot at present be classified as either a vadose or phreatic phenomenon, although it is probably a feature of secondary enlargement. It is the valley bar: the cave passages tend to pinch out, *i.e.,* the passage cross-section is reduced, as a valley is approached. This feature is observed in Level Crevice Cave between Whipsey Shaft and the Mining Room in Level A, where the passage passes beneath a small valley.

Water Analyses

Twenty-two sampling stations were set up within the cave in three general areas:

1) In the Level C stream between the dam and the Eastern Entrance,
2) In the passage east of Whipsey Shaft as far as the filled shaft in Level A, and

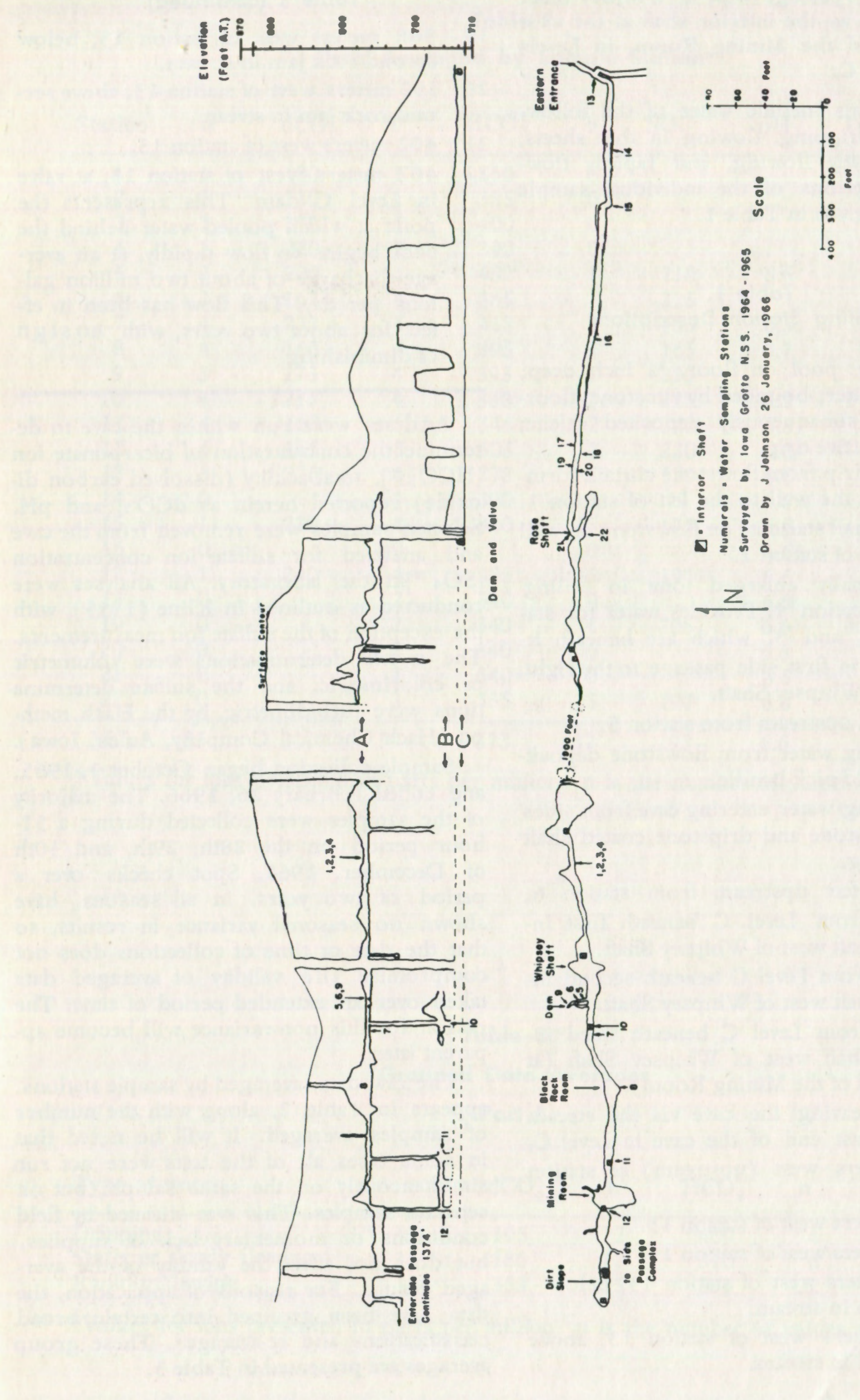

Figure 1. Map of Level Crevice Cave, Iowa.

3) In the passage west of Whipsey Shaft as far as the interior shaft at the west end of the Mining Room, in Levels A and C.

These stations include water of the following types: dripping, flowing in thin sheets, pooled, slowly flowing, and rapidly flowing. Descriptions of the individual sample stations are given in Table 1.

Table 1.
Sampling Station Descriptions

1	Shallow pool on floor, ¾ inch deep; clear water; bounded by rimstone; floored by subaqueously deposited calcite; fed by active drip.
2	Active drip from flowstone curtain forming on the wall to the left of station 1.
3	Very small stalactite on flowstone on wall to right of station 1.
4	Solutionally enlarged joint in ceiling above station 1. Provides water for stations 2 and 3, which are beneath it.
5	Stream in first side passage to the right, west of Whipsey Shaft.
6	Ten feet upstream from station 5.
7	Dripping water from flowstone deposited on old pick handle.
8	Dripping water entering cave from sides of flowstone and dripstone coated shaft in ceiling.
9	Fifteen feet upstream from station 6.
10	Water from Level C beneath first interior shaft west of Whipsey Shaft.
11	Water from Level C beneath second interior shaft west of Whipsey Shaft.
12	Water from Level C beneath third interior shaft west of Whipsey Shaft (at west end of the Mining Room).
13	Water leaving the cave via the stream at the east end of the cave in Level C.
14	59 meters west (upstream) of station 13.
15	118 meters west of station 13.
16	231 meters west of station 13.
17	369 meters west of station 13, below rock jam in stream.
18	370 meters west of station 13, above rock jam in stream.

Table 1 (continued)

19	388 meters west of station 13, below second rock jam in stream.
20	392 meters west of station 13, above second rock jam in stream.
21	402 meters west of station 13.
22	407 meters west of station 13, at valve in Level C dam. This represents the point at which pooled water behind the dam begins to flow rapidly, at an average discharge of about two million gallons per day. This flow has been in effect for about two years, with no sign of diminishing.

Analyses were run within the cave to determine the concentration of bicarbonate ion $[HCO_3^-]$, total acidity (dissolved carbon dioxide) reported herein as dCO_2, and pH. Selected samples were removed from the cave and analyzed for sulfate ion concentration $[SO_4^=]$in the laboratory. All analyses were conducted as outlined in Kline (1955), with the exception of the sulfate ion measurements. The *in situ* determinations were volumetric or colorimetric, and the sulfate determinations were turbidimetric, by the Hach method (Hach Chemical Company, Ames, Iowa).

Sample collection began October 1, 1965, and ended February 26, 1966. The majority of the samples were collected during a 51-hour period on the 28th, 29th, and 30th of December, 1965. Spot checks over a period of two years, in all seasons, have shown no seasonal variance in results, so that the date or time of collections does not compromise the validity of averaged data taken over an extended period of time. The reason for this non-variance will become apparent later.

The raw data, averaged by sample stations, appears in Table 2, along with the number of samples averaged. It will be noted that in some cases all of the tests were not run simultaneously on the same sample, but on separate samples. This was dictated by field conditions or momentary lack of supplies, but does not affect the validity of the averaged results. For reasons of application, the data have been grouped into certain broad classifications and re-averaged. These group averages are presented in Table 3.

Table 2.
Data Averaged by Sample Station*

Station	n	dCO_2	n	HCO_3^-	n	$SO_4^=$	pH	Temp., °C.
1	1	180	1	360	0			10
2	1	210	1	385	0			10
3	1	170	1	400	0			10
4	1	220	2	390	0			10
5	2	200	4	432	1	218	6.6	10
6	2	165	4	385	1	225		10
7	4	233	4	418	2	155	6.5	10
8	4	160	4	395	2	165	6.7	10
9	3	173	4	393	1	223		10
10	4	213	4	338	2	225	6.8	10
11	4	165	5	346	2	220	6.8	10
12	4	165	5	303	2	220	6.6	10
13	3	236	4	378	5	179	6.6	10
14	0		1	300	0		6.6	10
15	1	230	4	320	5	175	6.6	10
16	0		0		0		6.6	10
17	1	240	4	325	3	191	6.6	10
18	0		2	310	0		6.6	10
19	0		2	340	1	205	6.6	10
20	0		2	340	0		6.6	10
21	0		1	340	0		6.6	10
22	0		3	335	5	197	6.6	10
ALL	35	211	59	373	32	193	6.6	10

*Values for ions presented in parts per million. n is the number of values averaged.

Table 3.*
Grouped Data Averages
Part A

Type of water	n	dCO_2	n	HCO_3^-	n	$SO_4^=$
Dripping	12	195	12	409	4	160
Static or slowly flowing	11	186	12	310	6	222
Rapidly flowing	12	353	35	319	22	202

*Values for ions presented in parts per million. n is the number of values averaged.

Table 3.*

Part B

Station	n	dCO_2	n	HCO_3^-	n	$SO_4^{=}$	Flow direction of series
Descending water at Level A stations:							Toward lower levels
4	1	220	1	390	0		
2	1	210	1	385	0		
3	1	170	1	400	0		
1	1	180	1	360	0		
7	4	233	4	418	2	155	Drips
8	4	160	4	395	2	165	
Rapidly flowing water in Level A:							Downstream
9	3	173	4	393	1	223	
6	2	165	4	385	1	225	
5	2	200	4	432	1	218	
Static water in Level C:							
12	4	165	5	303	2	220	Toward East
11	3	171	3	346	2	220	
10	4	213	5	338	2	225	
Rapidly flowing water in Level C:							
22	0		3	335	5	197	Downstream
21	0		1	340	0		
20	0		2	340	0		
19	0		2	340	1	205	
18	0		2	310	0		
17	1	240	4	325	3	191	
16	0		0		0		
15	1	230	4	320	5	175	
14	0		1	300	0		
13	3	236	4	378	5	179	

*Values for ions presented in parts per million. n is the number of values averaged.

DETERMINATION OF SOLUTION REACTION

The two possible overall solution reactions are the carbonic acid reaction or, as suggested by Howard (1960), a sulfuric acid reaction. These are presented below as I and II respectively:

I) *Step A*

$$2\,H_2O + 2\,CO_2 \rightarrow 2\,H_2CO_3$$

Step B

$$2\,H_2CO_3 + Ca{\bullet}Mg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^{=}$$

Step A + Step B.

$$2\,H_2O + 2CO_2 + Ca{\bullet}Mg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^-$$

II) *Step A*

$$4\,FeS_2 + 15\,O_2 + 2H_2O \rightarrow 2\,Fe_2(SO_4)_3 + 2H_2SO_4$$

Step B

$$2Fe_2(SO_4)_3 + 12H_2O \rightarrow 4Fe(OH)_3\ 6H_2SO_4$$

Step C

$$4\,Fe(OH)_3 \rightarrow 2\,Fe_2O_3{\bullet}n\,H_2O$$

Step D

$$8\,H_2SO_4 + 8Ca{\bullet}Mg(CO_3)_2 \rightarrow 8\,Ca^{++} + 8Mg^{++} + 8\,SO_4^{=} + 16HCO_3^-$$

Step A + Step B + Step C + Step D

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O + 8\,Ca{\bullet}Mg(CO_3)_2 \longrightarrow 2Fe_2O_3{\bullet}n\,H_2O + 8Ca^{++} + 8Mg^{++} + 8SO_4^{=} + 16\,HCO_3^-$$

It is readily apparent that there is no sulfate ion present in the products of the carbonic acid reaction, whereas in the sulfuric acid reaction products sulfate ion is present, providing a ready method of differentiation between the two solution reactions. The data show (see Table 1) that sulfate ion is present in the cave waters in fairly large concentration. Furthermore, from the stoichiometry of the sulfuric acid reaction one would expect to find under ideal conditions that the concentration of the sulfate ion would be exactly half the concentration of bicarbonate ion. The overall data average (Table 2) agrees with this ideal ratio within four percent.

Including the observations that:

1) There is considerable pyrite and marcasite (both FeS_2) in the bedrock, including both disseminated and locally massive deposits (up to a maximum of 16% in one drill hole several miles south of the cave);
2) The dissolved oxygen in the water is at saturation at all times;
3) Analyses of the dolomite bedrock show between 0.9% and 2.3% limonite ($Fe_2O_3{\bullet}n\,H_2O$); and
4) There are no known sulfate ore bodies in the cave or in the local cave area (although some quite small deposits of barite are known in other areas of the quadrangle),

it becomes increasingly clear that the sulfuric acid reaction is occurring in Level Crevice Cave, and therefore locally in the Galena dolomite.

That the data do not vary seasonally also favors the sulfuric acid reaction. The lack of variance is due to the fact that the sulfuric acid reaction is independent of CO_2 production in the overlying soil and humus, but rather, is dependent only upon the amount of pyrite or marcasite which comes in contact with the oxygenated water, a factor which remains quite constant throughout the year.

The pathway given for the sulfuric acid reaction is a standard inorganic mechanism. However, the interesting possibility exists that the production of the sulfuric acid may be partially or completely organic, because large numbers of iron bacteria of the genera *Crenothrix* and *Gallionella* live in the cave. In some places, large colonies of these bacteria are prominent, as in the stream at stations 5, 6, and 9. These bacteria do not gain their energy by the normal mechanisms of photosynthesis or saprophytic dependence upon organic matter in the water, but by the oxidation of ferrous iron to ferric iron. These bacteria grow best in a dark aquatic environment which has ample amounts of ferrous iron and CO_2 dissolved in the water, at a temperature of 10°C. and a pH of 6.6, the exact conditions prevailing in the cave.

Therefore, it would seem logical that the bacteria could produce the sulfuric acid by the following summary reaction:

Step A (alternate)

$$4FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,H_2SO_4$$

The ferric hydroxide is then excreted by the bacterium into its surrounding medium, and undergoes the same simple rearrangement and loss of water as occurs in Step C of the inorganic mechanism (Cotton and Wilkinson, 1962).

The most striking fact about this mechanism is that the same number of moles of pyrite or marcasite and of oxygen and water are used as in the inorganic mechanism. Also, the same number of moles of sulfuric acid are produced. Therefore, at least in gross aspect, it makes no difference which mechanism is occurring, as the end result in terms of cave development is identical for both.

Considering the foregoing evidence, then, I have concluded that the sulfuric acid reaction is the major solution reaction occurring in Level Crevice Cave, and therefore, locally in the Galena dolomite.

THE DEPOSITION REACTION

One of the most interesting anomalies of the cave's chemistry is that when water enters the cave in Level A, it is capable of both dissolving more bedrock *and* depositing speleothemic material. This is indicated by the data averages from sample stations viewed on a vertical profile. Analyses of entering water taken from growing dripstone formations at stations 7 and 8 show about 73 percent of the sulfate ion content found in essentially static (in a vertical sense) water in Level C, at stations 10, 11, and 12, and in Level A, at stations 5, 6, and 9. This is interpreted as an indication that the water still dissolves bedrock between the time it enters the cave and it reaches its lowest point of progress, where the reaction stops due to lack of unoxidized pyrite and marcasite.

Yet we find at some stations in Level A that the water is depositing calcite. This apparent contradiction is a function of the relative solubilities of sulfates and bicarbonates at cave temperature, and of the partial pressure differential of CO_2, between the cave atmosphere and the water. The sulfates are highly soluble in water, are stable, and are independent of pCO_2, so that they are carried in solution the length of the cave, while the bicarbonates are relatively insoluble, unstable, and totally dependent on the pCO_2. Since the pCO_2 in the water is higher than that in the cave atmosphere, some of the bicarbonate decomposes to reach equilibrium by the usual inorganic reaction:

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

That this loss of CO_2 occurs and that deposition of calcium carbonate (calcite) occurs due to this loss is clearly demonstrated at stations 4 through 1 (see Table 3, Part B). Thus we see that solution and deposition occur by two different and essentially independent reactions, so that they can, and do, occur simultaneously within Level Crevice Cave.

Consideration of the combined stoichiometry of the solution and deposition reactions shows that one-half of the total amount of dissolved bedrock may be re-deposited as calcite, magnesite, or mixed-cation carbonates. In actual fact, a simple calculation based on the observed 3.33 percent loss of HCO_3^- between water entering at station 4 and exiting at station 13 shows that only 1.66 percent of the possible deposition occurs, due to the high pCO_2 in the cave atmosphere. This means that at present, approximately 0.83percent of the bedrock dissolved by the acidic water is re-deposited in the cave in the form of speleothems.

TRENDS IN THE CAVE CHEMISTRY

Upon inspection of the data averages, certain trends in both the solution and deposition reactions are observed as the water follows its course through the cave (see Table 3). These trends may be observed in both the horizontal and vertical dimensions.

Trends of the solution reaction:

It is evident that the solution reaction begins at the first point of contact of oxygenated water with bedrock containing pyrite or marcasite, and continues until either:

a) such contact is broken, or
b) the water ceases to move vertically and becomes pooled in areas where the pyrite and marcasite have been completely reacted to limonite by previous solution.

Case (a) is not observed in the cave, but is intuitively true. For instance, water leaving the cave at the Eastern Entrance is channeled off through a concrete storm sewer main, so that an indentical solution reaction obviously no longer continues. Case (b) is supported by the observation that dripping water entering Level A has a much lower $SO_4^=$ content than water which is pooled, as evidenced by the differences between stations 7 and 8 (see Table 3, Part B) and stations 12, 11, and 10 in Level C. That cessation of solution is a function of pooling, i.e., a halting of vertical movement, rather than a function of a limit upon depth of effective solution is indicated by:

1) The almost exact agreement of $SO_4^=$ data from the Level A stream (which is slowly flowing around a dam holding back pooled water) and from pooled water in Level C, and
2) The observation that slow horizontal flow seems to have little effect upon the solution reaction in Level C, as evidenced by the small changes between and among stations 12, 11, 10, and 22.

Trends of the deposition reaction:

As stated previously, calcite is deposited in any situation where the water is exposed to free air with a lower pCO_2 than that of the water. This should be true regardless of level or position within the cave, and is demonstrated by the existence of small speleothems in Level A and in Level C east of the Rose Shaft dam. However, the amount of carbonate deposited in any particular instance is quite small, as is the change in dCO_2.

One other interesting trend may be noted: after water leaves the valve at station 22, it progressively contains smaller amounts of sulfate ion as it flows rapidly outward in Level C. The reason for this removal of sulfate ion is not known. The dCO_2, pH, and HCO_3^- values remain essentially constant between the valve and the Eastern Entrance, indicating the $SO_4^=$ removal must be independent of these. Likewise, temperature of the water and the air also remain constant. One likely possibility exists that the many biological forms present in the stream may have representatives of the sulfur reducing bacteria among them, and that these account for the change, but to date no exact identifications have been made.

APPLICATIONS TO CAVE DEVELOPMENT

1) The wall rock of the upper two levels of the cave and of Level C east of the dam exhibit a brown to buff color characteristic of staining by limonite, whereas the rocks beneath Level C west of the dam exhibit a bluish-gray color, indicating that the pyrite and marcasite here have not been extensively oxidized to limonite. This places a lower limit on the depth at which solution via the sulfuric acid reaction has occurred of about 130 to 140 feet beneath the present land surface, and no more than 50 feet below the present water table. This limit is presumably controlled by the depth at which the oxygen content of the water becomes so low that the reaction ceases to function.

2) Howard (1960) demonstrates that the openings in which the ore minerals were deposited have been altered and enlarged by solution since mineralization. Yet the galena is not extensively oxidized, having been protected by a surface coating of cerrusite ($PbCO_3$). This means that enlargement of the crevices is accomplished via the sulfuric acid reaction using the FeS_2 exclusively, and explains the occurrence of sheets of unoxidized galena extending into open passage from ceiling joints.

3) The valley bar can best be explained by the sulfuric acid reaction. One would expect that if the carbonic acid reaction were occurring, the amount of rock dissolved would be greater in closer proximity to the surface, resulting in a larger passage rather than a smaller one. However, with the sulfuric acid reaction, the amount of acid produced varies directly with the amount of pyrite or marcasite encountered by the water, so that in general, up to the depth limit of effective solution of oxygen, the more bedrock that is traversed by the water, the more sulfuric acid is produced. Hence, a passage closer to the surface is necessarily smaller than a deeper one, and as a passage approaches a valley it pinches out.

4) Because the rate of solution does not vary seasonally, one would expect a cave of a given volume to form more rapidly via the sulfuric acid reaction. In addition, sulfuric acid is more highly dissociated in dilute aqueous solution than is carbonic acid, resulting in greater solution per mole of acid, and a more rapid rate of cave development. The speed of development and the continuation of solution may contribute to the "made-yesterday" appearance of solutional features in the cave, and almost certainly is responsible for the rapid production of the roof pendants and ceiling channels in Level B.

5) It appears that the morphologic phreatic and vadose indicator criteria normally in use for determining speleogenesis are the same regardless of the solution reaction involved, and that therefore, the origin of caves may still be interpreted in the usual manner, with the addition of the valley bar and any other peculiar features specficially due to the sulfuric acid reaction. As a corollary to this, it would seem that criticism of model experiments using sulfuric acid rather than carbonic acid to speed feature development is probably unfounded as long as the concentration of acid is kept within reasonable limits.

A SUMMARY — AND SOME SPECULATION

It has been conclusively demonstrated that at present, solution in Level Crevice Cave and locally in the Galena dolomite is accomplished predominantly by a reaction of the bedrock minerals with sulfuric acid, not carbonic acid. Deposition occurs simultaneously with solution by means of the normal reverse of the carbonic acid reaction, due to a pCO_2 differential between the water and free air. The maximum depth of solution is limited by the amount of dissolved oxygen in the water and position of the water table (if a water table is present), where the pyrite and marcasite have previously been oxidized. Deposition is independent of depth or position within the cave.

Certain aspects of the cave development, especially the valley bar, which require involved and clumsy combined chemical and hydro-mechanical explanations depending on the normal carbonic acid reaction, are especially clear cut and greatly simplified when the sulfuric acid reaction is known to occur.

The obvious, unanswered question at this point is concerned with the primary development of the cave. Did it develop via the sulfuric acid reaction mechanism? I think that it did. The suite of indicator criteria previously mentioned corresponds to that expected in formation of a cave under artesian flow conditions, as outlined by Howard (1964). To obtain these conditions at Dubuque, the Maquoketa Shale must have completely sealed off the top of the Galena dolomite except where youthful, steep valleys had been eroded by glacial meltwater. These valleys were relatively few in number. In this case there would have been little chance for the carbonic acid mechanism to occur, since water reaching the crevices would already have had more than ample time to reach equilibrium with respect to this reaction. However, it would still be saturated with oxygen. The action of the sulfuric acid reaction would not begin until it reached a pyrite-marcasite rich area, and would therefore not have commenced until the water reached Dubuque. In view of these conditions, and because there is no real evidence to the contrary, I feel justified in concluding that the sulfuric acid mechanism, in addition to being the proven mechanism of secondary enlargement, was also probably the primary enlargement or development mechanism.

It is interesting to speculate upon the extent of occurrence of this reaction in caves in other areas and in other bedrock, particularly limestones. Even taking for granted that the caves of the Dubuque area are located in bedrock having a high pyrite and marcasite content, and thus are somewhat a special case, many other dolomites and limestones contain at least some pyrite and marcasite, and, as is clear from inspection of the reactions, it does not take much sulfuric acid (or, therefore, much pyrite or much marcasite) to significantly affect cave development. It may be found through further detailed water analyses and observation of bedrock, both underground and in outcrop, that the reaction is more general than has been previously thought.

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Vertebrate Remains from the Dickson Limestone Quarry, Halton County, Ontario, Canada

By C. S. Churcher* and M. Brock Fenton**

ABSTRACT

A crevice cave in the Niagara Escarpment southwest of Milton, Ontario, has yielded remains of the painted turtle (*Chrysemys picta*), short-tailed shrew (*Blarina brevicauda*), smoky shrew (*Sorex fumeus*), big brown bat (*Eptesicus fuscus*), long-eared bat (*Myotis keenii*), little brown bat (*M. lucifugus*), red-backed vole (*Clethrionomys gapperi*), meadow vole (*Microtus pennsylvanicus*), red squirrel (*Tamiasciurus hudsonius*), deer mouse (*Peromyscus maniculatus*), muskrat (*Ondatra zibethicus*), and wapiti (*Cervus canadensis*). Because wapiti have been absent from the area since 1750 A.D., a minimum age of 215 years is suggested for the fauna.

LOCATION

The Dickson Limestone Quarry lies in Nelson Township, Halton County, Ontario, above the lip of the Niagara Escarpment southwest of Milton (fig. 1, insert), at Lat. 43° 26' N., and Long. 79° 54' W. The quarry was visited by both authors on 22 June, 1965, while running a survey of caves and quarries in the Niagara Escarpment lying between Waterdown and Highway 401 west of Milton.

NATURE OF DEPOSIT

The Dickson Quarry Cave was a crevice cave in the Lockport dolomite. The cave was exposed by the quarrying of the west wall leaving the east wall exposed on the face of the quarry. Evidences of a cave on the exposed surface were dripstone and stratified features observable from the other side of the quarry 300 feet away (fig. 1). Close examination of the cave wall revealed travertine or flowstone on the vertical faces, in places cementing stratified layers of reddish soil particles and small vertebrate bones (figs. 2, 3 and 4)), while in others similar stratified deposits were unconsolidated.

The stratified deposits in the Dickson Cave appear to have been formed on the floor of a crevice cave similar to the existing Mount Nemo Cave located about 600 yards south of the Dickson Quarry and described by Bateman (1960) and Ongley (1965). The presence of well separated stratified deposits lying at different levels above and below vertical flowstone sheets suggests a fluctuating water level. The chiropteran longbones within these upper stratified deposits all have their long axes oriented parallel to the rock face, which suggests that gentle currents of sufficient velocity to move the bones but not fracture them existed in the water within the cave, at least at some periods during the cave's history. The cave was at least 25 cm wide in places as detached stalagmitic or stalactitic nodules up to 20 cm in diameter were observed and some of the flowstone sheets were nearly 20 cm thick.

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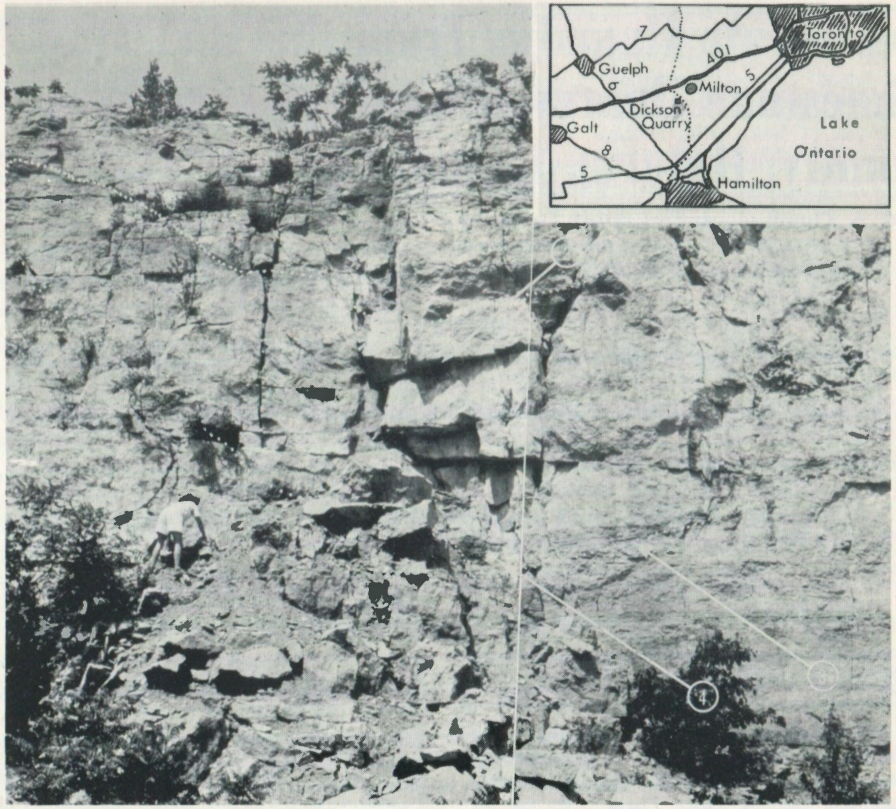

Figure 1.

Composite photograph of east wall of Dickson Quarry Cave, near Milton, Ontario, Canada. Dotted lines indicate approximate roof and floor levels of the cave. Arabic numerals refer to figures 2, 3 and 4. Figure at left gives scale. INSERT: Map showing location of the Dickson Quarry. Dotted line indicates the Niagara Escarpment. Numerals are highway numbers.

FAUNA

Class REPTILIA
Order CHELONIA

Chrysemys picta (Schneider), the painted turtle, was identified from the anterior part of a carapace, directly posterior to the anterior opening, and represented by all or part of six osteoderms. A second fragment of a carapace was also found and is assigned to *C. picta* although its exact location on the carapace is uncertain.

Class MAMMALIA
Order INSECTIVORA

Blarina brevicauda (Say), the short-tailed shrew, is represented by a right mandible with full dentition.

Sorex fumeus Miller, the smoky shrew, is represented by a right mandible with full dentition, and one ulna.

Order CHIROPTERA

Eptesicus fuscus (Beauvois), the big brown bat, is represented by a right mandible with two molars. This species was identified primarily on its size.

Myotis keenii (Merriam), three skulls of the long-eared or Keen's myotis each have an interorbital width of less than 4.0 mm (Table 1).

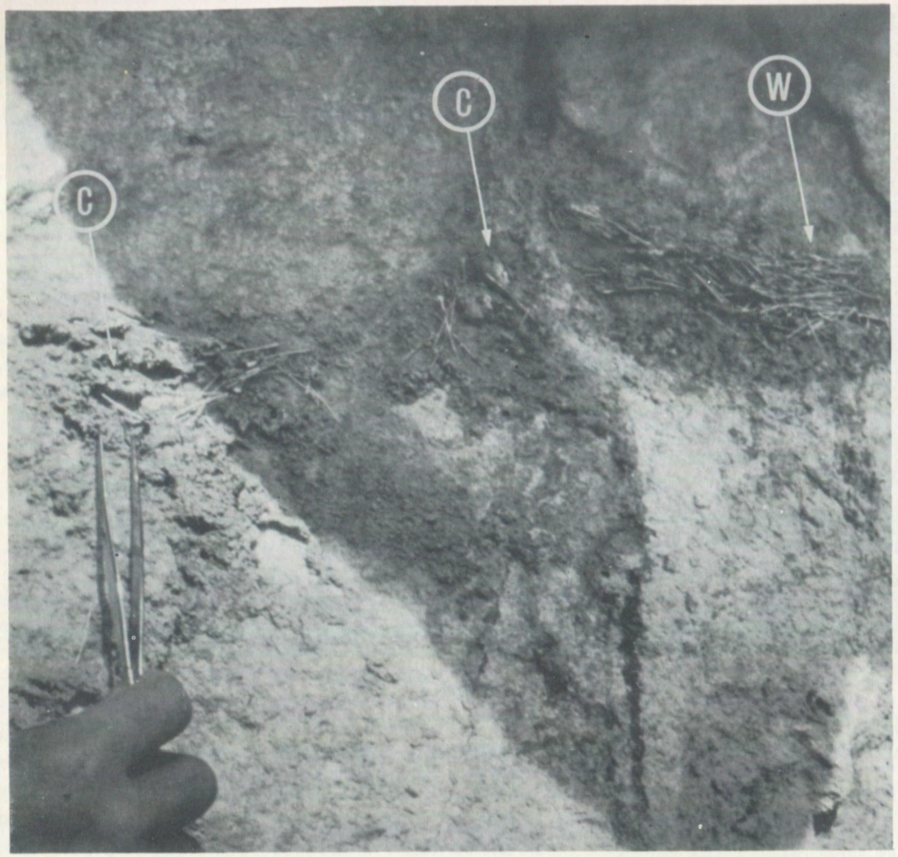

Figure 2.

Stratified and consolidated deposit protected by rock overhang and showing two crania (c) and many bones of the forearm (w) of chiropterans aligned by water currents. Hand and forceps in foreground.

Table 1.

MYOTIS skulls from Dickson Quarry, with data of M. LUCIFUGUS and M. KEENII from Miller and Allen (1928). All measurements in millimeters.

Dimension	DC1	DC2	DC3	DC4	*M. lucifugus*	*M. keenii*
Length overall	15.0	15.0	14.8	14.8	14.2-15.1	14.2-15.6
Interorbital width	3.60	3.65	4.00	3.55	4.00-4.20	3.40-4.00

Myotis lucifugus (LeConte), the little brown bat, is represented by one skull which had an interorbital width of 4.0 mm (Table 1, DC 3).

Other assorted bat remains were also found. They are listed below and measurements of the cubiti given in Table 2. These could derive from either *Myotis subulatus* or *Pipistrellus subflavus* as the measurements of the bones found correspond closely with those given for these species by Miller and Allen (1928), and Peterson (1966).

Figure 3.

Detail of dripstone-covered joint face with small nodular travertine concretions, smooth dripstone, and partially consolidated stratified deposits lying on the floor of Dickson Quarry Cave.

Table 2.
Lengths of the Dickson Cave MYOTIS cubiti, humeri and femora and a comparison of the cubiti with data of MYOTIS LUCIFUGUS, M. KEENII and M. SUBULATUS from Miller and Allen (1928) and PIPISTRELLUS SUBFLAVUS from Peterson (1966). All measurements are in millimeters.

Length overall	Measurements					Combined Range
Cubiti - left	33.2	32.9	34.0	33.7	33.1	
- right	34.6	34.4	35.6			32.9 - 35.6
Humeri - left	21.2	20.7	21.2	22.1		
- right	21.8	22.4	23.5			20.7 - 23.5
Femora - left	13.2	14.2				
- right	13.3	13.5	14.2			13.2 - 14.2

Comparisons of ranges of lengths of cubiti

Dickson Cave *Myotis*	32.9 - 35.6
Myotis lucifugus	35 - 40
M. keenii	34 - 38
M. subulatus	31 - 35
Pipistrellus subflavus	31 - 35

However, it is likely that they all derive from one of the species of *Myotis* identified from the skulls, possibly *M. keenii*.

The elements recovered are:–

- 16 mandibles, 9 left and 7 right, probably *Myotis* sp.
- 16 humeri, of which 7 were complete, 3 right and 4 left.
- 6 femora, 2 left, 3 right, and 1 incomplete.
- 17 cubiti (radio-ulnae), 8 of which were incomplete but identifiable, and 6 as fragments. Of the identifiable complete and incomplete and incomplete sepcimens, 7 were left and 3 right cubiti.
- 45 metacarpels, 8 of which were complete.
- 1 partial tibia.
- 1 complete innominate bone.
- 1 complete scapula.

Order RODENTIA

Clethrionomys gapperi (Vigors), the red-backed vole, is represented by a left and a right mandible.

Microtus pennsylvanicus (Ord), the meadow vole, is identified on a left mandible, a first lower molar, one tibia and one ulna.

Tamiasciurus hudsonius (Trouessart). One right mandible with no teeth appears to be from a red squirrel on the basis of size.

Peromyscus maniculatus (Wagner), the deer mouse, is represented by a right and a left mandible, and a partial left palate with two molars.

Ondatra zibethicus (Linnaeus). A third right metatarsal and a tail vertebra appear to be referrable to the muskrat.

Order ARTIODACTYLA

Cervus canadensis Erxleben, wapiti, is represented by a fragment from the posterior surface of the shaft of a left femur.

DISCUSSION AND AGE OF FAUNA

There are few references in the literature to Canadian late Pleistocene or Post-Wisconsin fossils of Insectivora, Chiroptera, or Rodentia. Weber (1955) reports the occurence of Pleistocene remains in a cave near Hamilton. Churcher & Karrow (1963) report *Tamias striatus* and *Microtus pennsylvanicus* from a soil horizon in the Scarborough bluffs, radiocarbon dated at 5,500 ± 70C14 years or about 3550 B.C. This is considered contemporary with the Hamilton Bay fauna described by Wetmore (1958) which includes *Pitmys pinetorum*. *Ondatra zibethicus* has also been added to this fauna (Churcher & Karrow, 1963).

Figure 4.

Two vertically separated, partially consolidated stratified deposits with smooth dripstone face between them illustrating evidence for fluctuating water levels. Geological hammer for scale.

The remains found in the cave were associated with some minute bits of charcoal and wood. No radiocarbon dating was attempted although a minimum age for the deposit may be suggested from the presence of the fragment of wapiti (*Cervus canadensis*), on the assumption that the other remains in the deposit are contemporary with the wapiti bone. Wapiti became extinct in Ontario about 1850 A.D. (Peterson, 1966). After 1750 A.D., wapiti were mainly confined to the Ottawa Valley (Peterson, 1957). This suggests a minimum age of 215 years for the deposit. Remains of wapiti have also been recovered from archaeological diggings on a Huron village site near Glen Williams, Esquesing Township, Halton County, which is believed to have been inhabited in the sixteenth century on the cultural evidence (Dr. H. G. Savage, Research Associate, Royal Ontario Museum, *pers. comm.*).

Prehistoric wapiti are also reported from other sites in Ontario:

Roebuck prehistoric village, Grenville Co. (Wintemberg, 1936).
Lawson prehistoric village, Middlesex Co. (Wintemberg, 1939).
Inverhuron site, Bruce Co. (Kenyon, 1957).
Petun village site, Collingwood Township, Grey County, dated 1600-1650 (Dr. H. G. Savage, *pers. comm.*).

The fauna present in the deposit is typical of a cave in this region. Muskrats, bats and deer mice have been observed in different caves throughout southeast Ontario (Fenton, 1965). The presence of the voles and the painted turtle is not unusual, since these animals are present in the area today (Peterson, 1966).

The stepped arrangement of the layers in the cave and the steepness of the walls and steps would make it very difficult for a quadruped to leave the cave once it was within it. The rodent and shrew remains might represent individuals trapped in this manner. The bat remains probably derive from hibernating bats which did not survive the winter and whose skeletons were preserved in the stalactitic pools. The presence of the fragment of wapiti femur may represent the remains of an Indian kill because a trail ran along the edge of the escarpment.

Subfossil chiropteran remains have not previously been reported from Canada. One may suspect that many of the other caves in southern Ontario described by Ongley (1965) may contain fossil or subfossil remains. The type of deposit reported from the Dickson Cave is usual in many caves, and an examination of other Ontario caves may reveal further small faunas of postglacial age.

ACKNOWLEDGEMENTS

We thank Dr. R. I. Peterson for checking the identification of some of the remains, and Dr. T. S. Parsons who confirmed the identification of *Chrysemys picta* and read the manuscript.

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A New Species of the Pseudoscorpion Genus, Aphrastochthonius (Arachnida, Chelonethida), from a Cave in Alabama*

By William B. Muchmore

ABSTRACT

A new species of the unique heterosphyronid genus, *Aphrastochthonius* Chamberlin, is described, based upon a specimen from Crystal Caverns, Jefferson County, Alabama.

In 1962 J.C. Chamberlin described a new genus and species of pseudoscorpion, *Aphrastochthonius tenax,* based upon one male and one female from Bangor Cave, Blount County, Alabama. Nothing more was known of this rare cavernicolous genus until Mr. Stewart B. Peck recently collected another individual in Crystal Caverns, Alabama, some 25 miles from Bangor Cave. The new specimen proved to belong to a species distinct from *Aphrastochthonius tenax.*

Aphrastochthonius pecki, new species
(Figs. 1-2)

Material: Holotype female (WM 873.01001) collected by S.B. Peck, 10 September 1965, in Crystal Caverns, Clay, Jefferson County, Alabama.

Description: Female: Generally similar to *Aphrastochthonius tenax* Chamberlin, but smaller and more robust. Carapace slightly longer than broad; epistomal process distinct, with irregular serrations; surface finely reticulated. No eyes or eye spots present. Carapace with 18 long, slender setae (4-4-4-2-4) and a microseta at each side of the anterior margin. Coxal area as in *A. tenax*; each coxa I with a curved row of seven, short, bilaterally pinnate spines, each coxa II with a row of eight similar spines. Small, bisetose intercoxal tubercle present.

Abdomen long ovate; surfaces of tergites marked with fine transverse lines; surfaces of sternites smooth; pleural membrane essentially smooth, but beset with numerous, tiny, triangular papillae. Tergal chaetotaxy 4:4:4:6:6:6:6:6:6:4:T2T:0. Sternal chaetotaxy 6:(3)7(3):(4)9(4): 12:11:11:11:8:T1T1T1T:0:—mm.

Chelicera slightly shorter than carapace; 2.3 times as long as broad. Palm with five setae, including only one accessory seta situated laterad of *b;* fixed finger with a row of eight medium-sized teeth plus a single large tooth at the distal end of the row; movable finger with a row of nine medium-sized teeth; galea represented by a very slight elevation of the finger margin; serrula exterior of 15-16 blades; flagellum of ten finely pinnate setae.

Palps like those of *A. tenax*, but less attenuate. Proportions of the segments shown in figure 1. Surfaces of all parts except fingers covered with very fine granules. Tactile setae of chela as indicated in figure 2. Fixed finger with a row of 15 widely-spaced, large, sharp teeth and two small, sharp denticles at the basal end of the row; movable finger with a row of nine similar, large teeth and a small, rounded, basal denticle. Trochanter 1.65, femur 5.7, tibia 2.0, chela 5.6 times as long as broad; hand 2.6 times as long as deep; movable finger 1.38 times as long as hand.

Legs of typical facies and rather slender. Leg IV with entire femur 2.9 and tibia 4.4 times as long as deep; tactile seta present on metatarsus, 0.46 the length of the segment from the proximal end.

Male: unknown.

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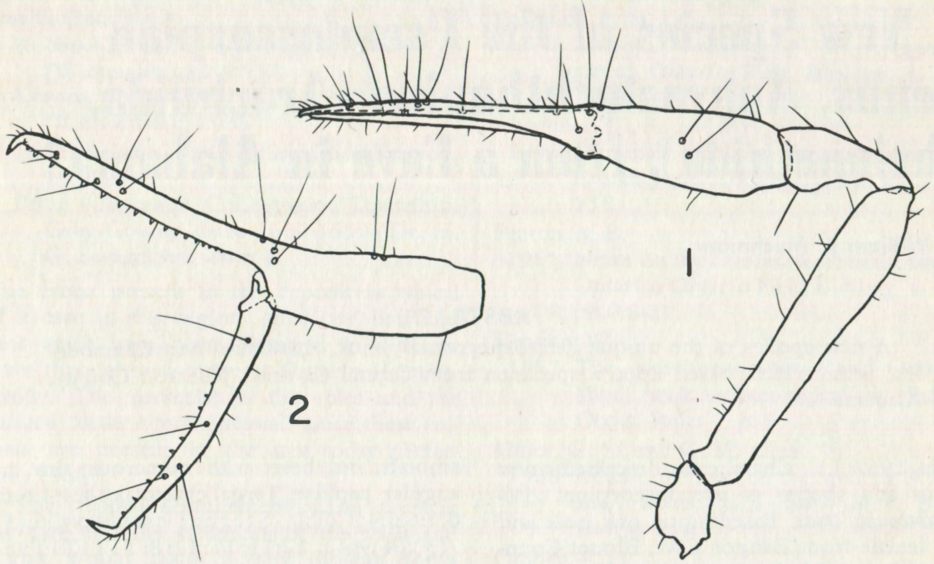

Figures 1 and 2.

Aphrastochthonius pecki, new species, holotype female. 1. Dorsal view of right palp. 2. Lateral view of left chela.

Measurements of holotype (mm.): Body length 1.36. Carapace 0.37 long by 0.35 wide. Chelicera 0.34 long by 0.15 broad; movable finger 0.18 long. Palpal trochanter 0.15 by 0.09; femur 0.57 by 0.10; tibia 0.22 by 0.11; chela 0.78 by 0.14; hand 0.34 by 0.13; movable finger 0.47 long. Leg I: basifemur 0.32 by 0.06; telofemur 0.16 by 0.05; tibia 0.155 by 0.05; tarsus 0.32 by 0.04. Leg IV: entire femur 0.45 long; basifemur 0.20 by 0.155; telofemur 0.30 by 0.14; tibia 0.31 by 0.07; metatarsus 0.15 by 0.06; telotarsus 0.33 by 0.04.

Remarks: The holotype female of *Aphrastochthonius pecki* has been compared directly with the allotype female of *A. tenax*, borrowed from the American Museum of Natural History. Though they are similar in many respects, *A. pecki* may be distinguished easily from *A. tenax* by its smaller size and less attenuated appendages. Further, *A. pecki* bears fewer teeth on the chelal fingers and has only five (rather than six) setae on the palm of the chelicera. It is pertinent to note here that the allotype of *A. tenax* actually has two setae on the intercoxal tubercle rather than one as reported by Chamberlin (1962, p 308).

Unfortunately, study of this new species of *Aphrastochthonius* sheds no new light upon the relationship of this genus to other genera of the Chthoniidae. It bears some resemblance to *Pseudochthonius*, especially in the possession of pinnate spines on coxae I and II, but differs from that genus in the possession of a bisetose, intercoxal tubercle and in the morphology of the chela. Elucidation of its relationships will probably depend upon further knowledge of the neotropical heterosphyronids.

The holotype will be deposited in the collection of the American Museum of Natural History.

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